

Impact of the *Prestige* oil spill on marsh soils: Relationship between heavy metal, sulfide and total petroleum hydrocarbon contents at the Villarrube and Lires marshes (Galicia, Spain)

Impacto de la marea negra del *Prestige* en suelos de marisma: relación entre los contenidos de metales pesados, sulfuros e hidrocarburos en las marismas de Villarrube y Lires (Galicia, España)

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Abstract

The objectives of this study were to determine the effect of the *Prestige* oil spill on the total petroleum hydrocarbons and heavy metal contents of soils in two marshes (Lires and Villarrube, Galicia, Spain) and the relationship between their oxidation-reduction potential and the solubility of heavy metals with sulfide and sulfate contents. Soil samples were taken from polluted and unpolluted areas and their petroleum hydrocarbon contents, heavy metal contents and other chemical characteristics were measured. The soils affected by the oil spill show remarkable contents of Cr, Cu, Ni, Pb and V. The Lires marsh soils are more affected by fuel oil than Villarrube marsh. The effects of the contaminating agents on the soils reach distances of up to 500 m from the coastline. In the first 400 m, there are important spatial variations because the fuel oil penetrated into the soils through tidal action and not directly. The Cr, Cu, Ni, Pb and V contents of polluted soils were between 50 and 200 times higher than those of their unpolluted counterparts and the background concentrations in Galician coastal sediments. In the case of Cr, Cu, Ni, Pb and V, their origin through the fuel oil was corroborated by the high correlation ($r > 0.90$) between the concentrations of these metals and the total petroleum hydrocarbon content of the polluted soils, which shows the combined addition of these metals through the fuel oil.

Key words: heavy metals, hydrocarbons, oil spill, marsh soils.

Resumen

Los objetivos de este trabajo fueron determinar el efecto de la marea negra del buque tanque *Prestige* en el contenido total de hidrocarburos y de metales pesados en suelos de dos marismas (Lires y Villarrube, Galicia, España) y la relación entre el potencial de oxidación-reducción y la solubilidad de los metales pesados con los contenidos de sulfuros y de sulfatos. Se tomaron muestras de suelos de las zonas contaminadas y no contaminadas y se determinaron diversas características químicas, el contenido total de hidrocarburos y de metales pesados. Los suelos afectados por la marea negra muestran contenidos destacables de Cr, Cu, Ni, Pb y V. Los suelos de la marisma de Lires están más afectados que los de la de Villarrube. Los efectos de los agentes contaminantes sobre los suelos llegan hasta distancias de 500 m de la línea de costa. En los primeros 400 metros existen importantes variaciones espaciales debidas a que el fuel penetró en el suelo a través de las oscilaciones mareales y no directamente. Las cantidades de Cr, Cu, Ni, Pb y V en los suelos contaminados son de entre 50 y 200 veces mayores que las de los no contaminados y que los niveles de fondo de los sedimentos costeros de Galicia. La estrecha correlación positiva establecida entre los contenidos de metales pesados en los suelos y entre el contenido total de hidrocarburos y el de metales pesados ($r > 0.9$) muestra el aporte conjunto de los metales a través del fuel.

Palabras clave: metales pesados, hidrocarburos, marea negra, marismas, suelos.

Introduction

Marshes are an important part of fluvial, estuarial and coastal ecosystems. The short-term effects of fuel oil on marshes depends primarily on the vegetative responses. The adverse effects of oil on plants range from reductions in transpiration and carbon fixation to plant mortality (Pezeshki *et al.*, 2000), and the long-term effects depend more on the response of the soil microbial community that controls the remineralization of nutrients, soil redox potential and fuel oil degradation (Nyman and Patrick, 1995). The response of the soil microbial community may be influenced by the content of heavy metals in the marsh soils.

The Villarrube (4°23'40" W, 43°38'10" N) and Lires (9°15'06" W, 43°00'08" N) marshes are located in northwestern Galicia (Spain), in the estuaries of the rivers Ferrerías (Cedeira Ría) and Castro (Lires Ría), respectively. Both marshes were considered ecosystems that had not been negatively affected by human action (Fernández-Feal, 1999; Marcet *et al.*, 2000).

Low bulk densities, high organic matter content and high sulfide content often characterize tidal marsh soils (Griffin and Rabenhorst, 1989; Fernández-Feal, 1999; Marcet *et al.*, 2000; Andrade *et al.*, 2002). The organic matter accumulated by superficial deposition of marsh grass detritus and urban effluents is very important to the fate of trace metals (Griffin and Rabenhorst, 1989). The oxidation status of soils and sediments affects the distribution of some trace metals among bound, unavailable, soluble and available forms (Gambrell *et al.*, 1991).

The combination of anaerobic conditions and high organic matter content makes the salt marsh environment ideal for bacterial reduction of sulfates to sulfides (Pons and Van Breemen, 1982). This process plays an important role in the development of marsh sediments and in the control of heavy metal solubility.

This paper reports the effects of the *Prestige* oil spill on the hydrocarbon and heavy metal contents of the soils of two affected estuarine environments two weeks after the spill had occurred.

Material and methods

One sample of emulsified fuel oil was taken from the sea and another two from each marsh. The fuel oil characterization and analytical methods are described briefly in table 1.

The soil sampling sites extended 750 m from the coastline during low tide (fig. 1). Six soil samples (Thionic Fluvisol) were taken during low tide at each marsh (samples V and L) two weeks after the spillage and immediately after cleaning the beaches, one sample every 100 m and two controls (at 750 m, control L and control V). The sampling sites were chosen to obtain a representative measure of the pollution conditions in the marshes.

Topsoil (0–30 cm) samples were collected using an Eijkelpamp sampler and the samples were stored in polyethylene bags in darkness at 4°C. Five samples of each site

Introducción

Las marismas son una parte importante de los ecosistemas fluviales, estuarinos y costeros. Los efectos a corto plazo del fueloil en las marismas dependen principalmente de respuestas vegetativas, ya que los efectos nocivos sobre las plantas varían desde reducciones en la transpiración y en la fijación de carbono hasta la mortalidad (Pezeshki *et al.*, 2000), mientras que a largo plazo, dependen más de la respuesta de la comunidad microbiana del suelo que controla la remineralización de nutrientes, el potencial red-ox del suelo y la degradación del fuel (Nyman y Patrick, 1995). Esta respuesta depende, en parte, del contenido de metales pesados en suelos de marisma.

Las marismas de Villarrube (4°23'40"W, 43°38'10"N) y Lires (9°15'06"W, 43°00'08"N) se localizan en el noroeste de Galicia (España), en los estuarios de los ríos Ferreras (Ría de Cedeira) y Castro (Ría de Lires), respectivamente. Ambas se consideraban como no afectadas negativamente por la acción antrópica (Fernández-Feal, 1999; Marcet *et al.*, 2000).

Los suelos de marismas mareales están caracterizados frecuentemente por densidades bajas y contenidos altos de materia orgánica y de sulfuros (Griffin and Rabenhorts, 1989; Fernández-Feal, 1999; Marcet *et al.*, 2000; Andrade *et al.*, 2002). La materia orgánica, acumulada por deposición superficial de restos vegetales de la marisma y por aportes de diversos efluentes urbanos, es fundamental en el comportamiento de los metales pesados (Griffin y Rabenhorts, 1989). El estado de oxidación de los suelos y sedimentos afecta a la distribución de algunos metales pesados entre formas enlazadas, no asimilables, solubles y disponibles (Gambrell *et al.*, 1991).

La combinación de condiciones anaeróbicas y elevados contenidos de materia orgánica hace de las marismas salinas el ambiente idóneo para la reducción bacteriana de sulfato a sulfuro (Pons y Van Breemen, 1982). Este proceso juega un papel importante en el desarrollo de los sedimentos de la marisma y en el control de la solubilidad de metales pesados.

En este trabajo se presentan los efectos de la marea negra del *Prestige* sobre el contenido de hidrocarburos y de metales pesados de los suelos en dos ambientes estuarinos afectados, dos semanas después del vertido.

Material y métodos

Se tomaron tres muestras de combustible emulsionado, una en el mar y una en cada marisma. La caracterización del fuel y los métodos analíticos utilizados figuran, brevemente descritos, en la tabla 1.

Los lugares de muestreo se extendieron hasta 750 metros de distancia de la línea de costa en bajamar (fig. 1). Se tomaron seis muestras de suelos (Fluvisoles tiónicos) en cada marisma (muestras V y L), una cada 100 metros, y dos controles (a 750 m, control L y control V) dos semanas después del vertido e inmediatamente después de limpiar las playas. Los sitios de muestreo fueron elegidos para obtener una medida representativa de la contaminación en las marismas.

were taken at each sampling point. The samples from each site were air-dried, passed through a 2-mm sieve, mixed and homogenized in the laboratory. Subsequently, five subsamples from each aggregate sample were taken.

Redox potential (Eh) was measured on site, using a platinum electrode and a calomel reference electrode. Both electrodes were introduced into the topsoil to a depth of 15–20 cm. Ten measurements were made at each sampling site, and the results are the average of all of them. The Eh was measured based on a standard hydrogen reference electrode.

Sulfide was determined starting from the difference between the iron extracted with hydrochloric acid and nitric acid (Tabatabai, 1982), and the adsorbed $S-SO_4^{-2}$ was extracted with a solution containing $LiCl_2$ 0.1M and P (500 mg L^{-1}) (Tabatabai, 1982). Both were analyzed by turbidimetry with barium acetate.

The available content of Cr, Cu, Ni, Pb and V was extracted by the DTPA method developed by Lindsay and Norwell (1978). Total contents were extracted by acid digestion using a mixture of concentrated nitric, hydrochloric and hydrofluoric acids (1:3:3 v/v) in Teflon reactors placed in a microwave oven (Marcet *et al.*, 1997).

The analysis of Cr, Cu, Ni, Pb and V was carried out by ICP-OES (Perkin-Elmer Optima 4300 DV).

The efficiency of the extraction and analysis procedures was controlled by analyzing international standard reference material of marine sediment from estuaries such as MESS-3 (10 repetitions for each element) from the Marine Analytical Chemistry Standards Program of the Canadian National Research Council (Ottawa, Canada); the procedure is described in Marcet *et al.* (1997). MESS-3 is estuarial sediment characterized by a low average metal concentration, making the sediments an appropriate tool for the analytical control of the samples from the Galician marshes. The confidence intervals of the values obtained were similar to those certified by the Canadian National Research Council (table 2).

Total petroleum hydrocarbon content (TPH) was determined by the ISO/TR 11046 (E) (1994) procedure, proposed by RIZA (1980, 1987), Pennings (1987) and Weisman (1998). The soil samples, obtained in the field and stored in darkness at 4°C, were chemically dried with a hygroscopic salt, crushed and then extracted with 1,1,2-trichloro-1,2,2-trifluoroethane, adding magnesium silicate and shaking to remove the polar compounds. For quantitative determination, the extract was added to hexane and analyzed by gas chromatography. For detection, a flame ionization detector was used. The total petroleum hydrocarbon content of the samples was calculated using an external standard prepared with a mixture of n-alkane standard with carbon numbers between C_6 and C_{36} (Weisman, 1998).

The data were statistically analyzed and the least significant differences (LSD), at 5% level, used to separate means. The relationship between the different variables was evaluated by a simple correlation and regression analysis (Neter *et al.*, 1996).

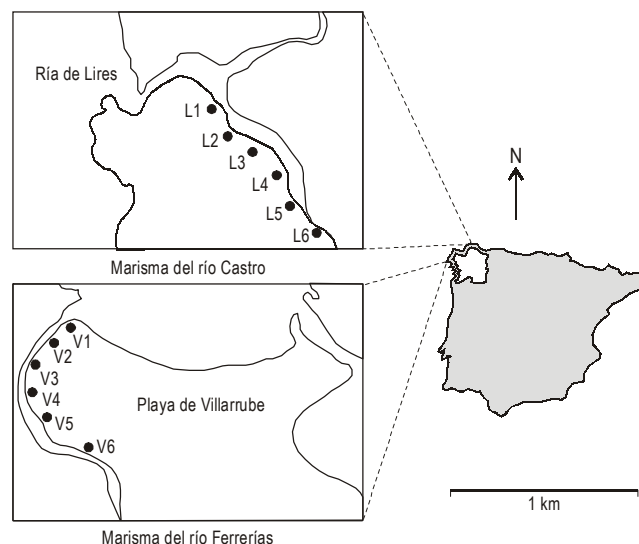


Figure 1. Villarrube and Lires marshes (Galicia, Spain). Location of the sampling sites.

Figura 1. Marismas de Villarrube y Lires. Localización de los sitios de muestreo.

Se tomaron seis muestras superficiales de los suelos (0–30 cm) en cada punto de muestreo, utilizando un muestreador Eijkelpamp. Las muestras se guardaron en bolsas de polietileno en ausencia de luz y refrigeradas a 4°C. En el laboratorio, se secaron al aire, se tamizaron por malla de 2 mm, se mezclaron las cinco muestras de cada sitio y se homogeneizaron. De esta mezcla homogénea se tomaron cinco submuestras para realizar los análisis.

El potencial red-ox se determinó *in situ* con un electrodo de platino y otro de referencia de calomelanos, que se introdujeron en la superficie de cada suelo hasta la profundidad de 15–20 cm, y se evaluó utilizando, como base, el electrodo de referencia de hidrógeno. Se realizaron diez medidas en cada punto de muestreo y los resultados son la media de estas determinaciones.

El contenido de sulfuro fue determinado por diferencia entre el hierro extraído con ácido clorhídrico y ácido nítrico (Tabatabai, 1982) y el $S-SO_4^{-2}$ adsorbido se extrajo con una disolución de $LiCl_2$ 0.1M y P (500 mg L^{-1}) (Tabatabai, 1982). Ambos fueron analizados por turbidimetría con acetato bórico.

El contenido disponible de Cr, Cu, Ni, Pb y V se extrajo por el método del DTPA desarrollado por Lindsay y Norwell (1978). El contenido total se extrajo mediante digestión con una mezcla de ácidos nítrico, clorhídrico y fluorhídrico (1: 3: 3 v/v) en reactores de teflón en un horno de microondas (Marcet *et al.*, 1997). El análisis de Cr, Cu, Ni, Pb y V fue realizado por ICP-OES (Perkin Elmer Optima 4300 DV).

La eficacia del procedimiento de extracción y análisis fue controlada analizando un sedimento marino de referencia como el MESS-3 (10 réplicas para cada elemento), procedente del Programa de Estándares de Química Analítica Marina del *Canadian National Research Council* (Ottawa, Canada), y con el procedimiento descrito en Marcet *et al.* (1997). MESS-3 es

Table 1. Analytic data of the emulsified fuel oil and analysis methods.
Tabla 1. Datos analíticos del fuel emulsionado y metodología utilizada.

	Method	Units	Sample and sampling site					
			1. Open sea (vacuum-dried)	1. Open sea (moist)	2. Villarrube marsh (vacuum-dried)	2. Villarrube marsh (moist)	3. Lires marsh (vacuum-dried)	3. Lires marsh (moist)
Density (15C)	ASTM D 198 (1995)	kg m ⁻³	977a	988a	979a	988a	979a	979a
S	ASTM D 4239.Met C (1995)	g kg ⁻¹	28.3a	12.68a	23.2b	9.22b	24.8b	9.21b
C	ASTM D 4239.Met C (1995)		830.22a	371.94a	790.99b	314.66b	790.25b	293.49c
H ₂ O	Drying at vacuum ASTM D 95 (1995)	% (v/v)	—	55.20a	—	54.26a	—	55.20a
Ashes	ASTM D 482 (1995). Digestion with HNO ₃	g kg ⁻¹	—	4.23b	—	1.55c	—	5.17a
Cr	ASTM D 3605 (1995). Analysis by ICP-OES Digestion with HNO ₃	mg kg ⁻¹	8.67b	u.l.	7.06c	0.19b	11.33a	8.50a
Cu	ASTM D 3605 (1995). Analysis by ICP-OES Digestion with HNO ₃		14.09b	7.73b	18.16a	15.00a	10.78c	8.24b
Fe	ASTM D 3605 (1995). Analysis by ICP-OES Digestion with HNO ₃		176.10a	39.80c	163.83b	141.18a	61.21c	56.86b
Ni	ASTM D 3605 (1995). Analysis by ICP-OES Digestion with HNO ₃		42.01b	27.20b	50.65ab	30.80ab	55.95a	35.58a
Pb	ASTM D 3605 (1995). Analysis by ICP-OES Digestion with HNO ₃		12.58a	6.73b	9.41b	8.33a	6.27c	0.73c
Zn	ASTM D 3605 (1995). Analysis by ICP-OES Digestion with HNO ₃		4.91c	0.67b	9.41a	3.89a	7.97b	3.52a
V	ASTM D 3605 (1995). Analysis by ICP-OES		95.79b	58.93b	110.59ab	70.19a	125.62a	73.03a

u.l.: undetectable level. For moist or vacuum-dried samples, values of the same parameters followed by a different letter are significantly different ($P < 0.05$).

Table 2. Control of the efficiency of the method of extraction and determination of metals in a reference material (MESS 3).
Tabla 2. Control de la eficiencia del método de extracción y determinación de metales en un material de referencia (MESS 3).

Metal	Certified value (mg kg ⁻¹)	Analyzed value (mg kg ⁻¹)
Cr	105 ± 4	108 ± 8
Cu	33.9 ± 1.6	31 ± 5
Ni	46.9 ± 2.6	42.4 ± 6
Pb	21.1 ± 0.7	23.6 ± 2.5
V	243 ± 10	232 ± 14

Average and deviation standard of ten samples. Limit of tolerance and precision 95%.

Results and discussion

The heavy metal contents in the soils of both marshes are higher than the normal levels from petrogenic origin in these zones (tables 3, 4) (Marcet *et al.*, 1997; Fernández-Feal, 1999; Carballeira *et al.*, 2000; Marcet *et al.*, 2000), which seems to indicate the effect of the oil spill on these soils.

Polluted soils had significantly higher values than control soils ($P < 0.05$) with respect to total Cr, Cu, Ni, Pb and V contents. The heavy metal concentrations found in the polluted soils also exceeded the average concentrations in unpolluted Galician coastal sediments and soils (Barreiro *et al.*, 1988, 1994; Marcet *et al.*, 1997; Fernández-Feal, 1999; Carballeira *et al.*, 2000; Marcet *et al.*, 2000) and the background levels (table 3) (Barreiro *et al.*, 1988, 1994; Carballeira *et al.*, 2000). The highest levels were found at Lires marsh, yielding evidence in the sense that this marsh was more affected by the fuel than the Villarube one.

The combined addition of these metals through the fuel oil seems to be corroborated by the significant positive correlation between the total heavy metal content with TPH content ($r > 0.90$, $P < 0.01$) in all cases (fig. 2), and also significant mutual correlation ($r > 0.90$, $P < 0.01$) (table 5) among total Cr, Cu, Ni, Pb and V levels (table 5).

DPTA-extractable metal contents were likewise low in relative terms (table 4). The predominance of insoluble forms is attributable to the low Eh values of these soils, and hence partly, in the case of the polluted soils, to their TPH contents (table 4).

The differences in heavy metal content in the soils are not related to their nature and properties (grain-size, organic matter content).

The relationship established between the oxidation-reduction potential and the sulfide content, and between the latter and the total contents of Cr, Cu, Ni, Pb and V (figs. 3, 4) shows that when there is a larger reduction the metal contents increase because they remain in the soil as precipitated sulfides. A significant negative relationship between the oxidation-reduction potential and the total content of hydrocarbons has also been established (fig. 5, $r = -0.9$, and significant for $P < 0.01$), which probably indicates that the fuel oil causes anaerobiosis and prevents the sulfide oxidation to sulfate and the heavy metals mobilization.

So, the redox potential has a decisive effect on the amount of Cr, Cu, Ni, Pb and V in insoluble form. Table 4 shows that the highest concentrations occur under reduced conditions, gradually decreasing when they change to oxidant values. Gambrell *et al.* (1991) found that soluble heavy metals were hardly affected by the oxidation-reduction potential except at intermediate oxidation-reduction potentials similar to those found in the soils studied in this paper.

However, the scarce amount of $S-SO_4^{2-}$ and metals in available form (table 4) shows that when oxidation is produced by the fluctuation of the tide, or desiccation, a great proportion of these metals will become easily soluble forms, which can

un sedimento de estuario caracterizado por una concentración metálica media-baja que lo hace una herramienta adecuada para el control analítico de muestras de las marismas de Galicia. Los intervalos de confianza de los valores obtenidos son similares a los certificados por el *Canadian National Research Council* (tabla 2).

El contenido total de hidrocarburos (TPH) fue determinado por el método ISO/TR 11046 (E) (1994), propuesto por RIZA (1980 y 1987), Pennings (1987) y Weisman (1998). Las muestras de suelo tomadas en el campo y almacenadas a 4°C, se secaron químicamente con una sal higroscópica, fueron molidas y después extraídas con 1,1,2-tricloro-1,2,2-trifluoroetano; se les añadió silicato magnésico y se agitaron para eliminar los compuestos polares. Al extracto se añadió hexano para la determinación cuantitativa, y se analizó por cromatografía gaseosa. Para la detección, se utilizó un detector de ionización de llama. El contenido en la muestra se calculó utilizando un estándar externo preparado con una mezcla de estándares de n-alcenos con números de átomos de carbono de entre C_6 y C_{36} (Weisman, 1998).

Los datos fueron analizados estadísticamente. Se utilizó el test de diferencias significativas (DMS) al 5%. Se evaluó la relación entre las distintas variables mediante análisis de correlación y regresión (Neter *et al.*, 1996).

Resultados y discusión

El contenido de metales pesados en los suelos de ambas marismas es mayor que el nivel de origen petrogénico en esas zonas (tablas 3 y 4) (Marcet *et al.*, 1997; Fernández-Feal, 1999; Carballeira *et al.*, 2000 y Marcet *et al.*, 2000), lo cual parece indicar el efecto de la marea negra.

Los suelos afectados por el vertido tienen mayores contenidos de Cr, Cu, Ni, Pb, V e hidrocarburos (tabla 4) que los suelos control. Los contenidos de metales pesados en los suelos estudiados exceden los valores de niveles de fondo en sedimentos costeros (table 3) (Barreiro *et al.*, 1988, 1994; Carballeira *et al.*, 2000) y las concentraciones medias en sedimentos y suelos costeros gallegos no contaminados (Barreiro *et al.* 1988, 1994; Marcet *et al.*, 1997; Fernández-Feal, 1999; Carballeira *et al.*, 2000; Marcet *et al.*, 2000).

La marisma de Lires está más afectada por el fuel que la de Villarube, lo cual se manifiesta con mayores contenidos de metales pesados y de hidrocarburos en la primera de ellas.

El aporte conjunto de estos metales pesados a los suelos a través del fuel parece corroborarse por la estrecha y significativa correlación positiva existente entre el contenido total de metales pesados y de hidrocarburos (fig. 2; $r > 0.9$, significativo para $P < 0.01$) y también por la estrecha correlación entre los contenidos totales de los distintos metales pesados ($r > 0.9$, significativo para $P < 0.01$) (tabla 5).

Los contenidos de metales pesados extraíbles con DTPA son relativamente bajos (tabla 4). La predominancia de formas insolubles es atribuible a los bajos valores de Eh de los suelos afectados por la marea negra y, por tanto a su contenido total de hidrocarburos (tabla 4).

Table 3. Background levels in sediments and natural heavy metal contents in marsh soils (from Barreiro et al., 1988, 1994; Marcet et al., 1997; Fernández-Feal, 1999; Carballeira et al., 2000; Marcet et al., 2000).
Table 3. Niveles de fondo en sedimentos y contenido natural de metales pesados en suelos de marisma. (Barreiro et al., 1988 y 1994, Marcet et al., 1997; Fernández-Feal, 1999; Carballeira et al., 2000 y Marcet et al., 2000).

Sample and marsh	Distance to coastline during low tide (m)	Cr		Cu		Ni		Pb		V	
		Total	Available	Total	Available	Total	Available	Total	Available	Total	Available
V-1	0	48	u.l.	62	2	30	3	58	2	9	u.l.
V-3	200	36	u.l.	33	u.l.	11	u.l.	22	u.l.	4	u.l.
V-5	400	12	u.l.	21	u.l.	2	u.l.	6	u.l.	2	u.l.
L-1	0	53	2	50	3	16	2	11	1	3	u.l.
L-3	200	21	1	23	u.l.	6	u.l.	6	u.l.	2	u.l.
L-5	400	9	u.l.	5	u.l.	2	u.l.	2	u.l.	2	u.l.
Background levels in sediment from Galicia coast		25	-	25	-	7	-	20	-	-	-

u.l.: undetectable level

Table 4. Effect of the fuel oil on the different chemical characteristics of the marsh soils.
Tabla 4. Efecto del fuel en diferentes características químicas de los suelos de marisma.

Sample and marsh	Distance to coastline in low tide (m)	Eh (mV)	Adsorbed S-SO ₄ ⁼	S ⁻² -S	Total Cr		Total Cu		Total Ni		Total Pb		Total V		Total Hydrocarbon (g kg ⁻¹)
					Avail. Cr	Total Cr	Avail. Cu	Total Cu	Avail. Ni	Total Ni	Avail. Pb	Total Pb	Avail. V	Total V	
V-1	0	-173hi	109bc	123a	62b	27ab	271b	4cd	306b	7d	274b	7b	183bc	34b	97.3b
V-2	100	-84g	103c	8.1f	48c	10c	166c	6c	186c	8d	198c	2c	168cd	21c	78.1bc
V-3	200	-162hi	98c	112ab	61b	23b	284b	4cd	302b	6d	272b	8b	176c	34b	104.2b
V-4	300	-58f	143b	74c	26d	7c	142c	4cd	171c	6d	121d	13a	96e	16d	66.8c
V-5	400	-57f	161ab	73c	23d	7c	142c	5cd	161c	7d	94e	8b	87ef	16d	32.1d
V-6	500	53c	21e	21e	12de	2d	10e	8c	23e	11c	5h	2c	30gh	9e	6.2f
Control-V	750	170a	11f	1g	4f	0.5e	u.l.	1e	7f	1e	1i	u.l.	8h	1f	u.l.
L-1	0	-181j	90cd	121a	80a	36a	361a	23a	381a	27a	299a	8b	239a	43a	116.5ab
L-2	100	-150h	114bc	101b	64b	21b	298b	14b	309b	17b	220bc	11a	201b	31b	86.2bc
L-3	200	-174hi	81cd	113ab	76ab	31a	357a	20a	371ab	25a	280ab	8b	229ab	43a	148.4a
L-4	300	-53f	186a	62cd	23d	6c	134c	6c	157c	9d	40f	6bc	147d	21c	76.9c
L-5	400	-9e	101c	54d	16de	4cd	94d	6c	113d	8d	40f	5bc	68f	19c	47.2cd
L-6	500	26d	89cd	31de	7e	2d	98d	3d	104d	4de	20g	3c	41g	8e	9.3e
Control-L	750	142b	16ef	3g	2f	1de	2f	1e	2g	1e	u.l.	u.l.	6h	1f	2.3g

u.l.: undetectable level. In each column, values followed by different letters in each column differ significantly with $P < 0.05$.

Table 5. Pearson correlation matrix.
Tabla 5. Matriz de correlación de Pearson.

	Distance	Total Cr	Avail. Cr	Total Cu	Avail. Cu	Total Ni	Avail. Ni	Total Pb	Avail. Pb	Total V	Avail. V	S ² -S	Total Hydrocarbon
Distance	1	-0.89**	-0.81**	-0.87**	-0.58*	-0.89**	-0.63*	-0.88**	-0.65*	-0.93**	-0.89**	0.60*	-0.86**
Total Cr	-0.89**	1	0.978**	0.97**	0.75**	0.97**	0.77**	0.98**	0.58*	0.97**	0.96**	0.68*	0.93**
Avail. Cr	-0.81**	0.97**	1	0.96**	0.76**	0.95**	0.77**	0.95**	0.55*	0.91**	0.95**	#	0.89**
Total Cu	-0.87**	0.97**	0.96**	1	0.74**	0.99**	0.76**	0.95	0.68**	0.96**	0.97**	0.80**	0.94**
Avail. Cu	-0.58*	0.75**	0.76**	0.74**	1	0.72**	0.99**	0.60*	0.42	0.73**	0.76**	#	0.69**
Total Ni	-0.89**	0.97**	0.95**	0.99**	0.72**	1	0.74**	0.95**	0.70**	0.96**	0.98**	0.83**	0.94**
Avail. Ni	-0.63*	0.77**	0.77**	0.76**	0.99**	0.74**	1	0.63*	0.45	0.76**	0.79**	#	0.72**
Total Pb	-0.88**	0.98**	0.95**	0.95**	0.60*	0.95**	0.63*	1	0.59*	0.92**	0.92**	0.67*	0.91**
Avail. Pb	-0.65*	0.58*	0.55*	0.68**	0.42	0.70**	0.453	0.59*	1	0.62*	0.64*	#	0.64*
Total V	-0.93**	0.97**	0.91**	0.96**	0.73**	0.96**	0.76**	0.92**	0.62*	1	0.96**	0.66*	0.96**
Avail. V	-0.89**	0.96**	0.95**	0.97**	0.76**	0.98**	0.79**	0.92**	0.64*	0.96**	1	#	0.96**
S ² -S	0.60*	0.68*	#	0.80**	#	0.83**	#	0.67*	#	#	#	1	0.68*
Total hydrocarbon	-0.86**	0.93**	0.89**	0.94**	0.69**	0.94**	0.72**	0.91**	0.64*	0.96**	0.96**	0.68*	1

* Significant at 0.05 level. ** Significant at 0.01 level. # Not correlated

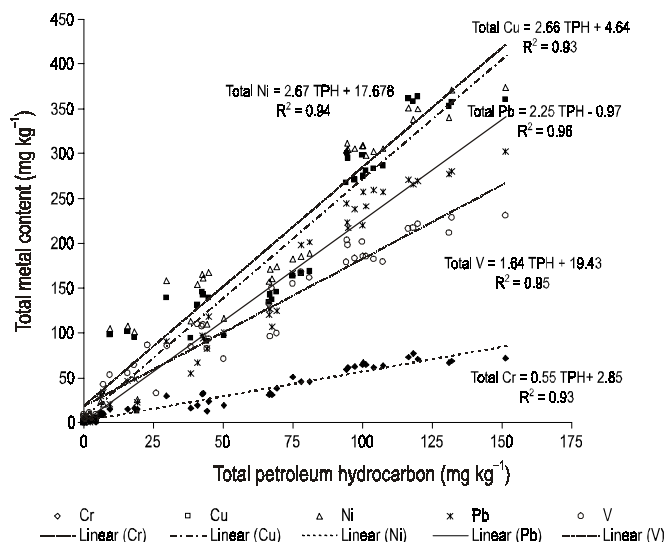


Figure 2. Variation of the total heavy metal content with the total petroleum hydrocarbon content. Regression and determination coefficient.

Figura 2. Variación del contenido total de metales pesados con el de hidrocarburos. Regresión y coeficiente de determinación.

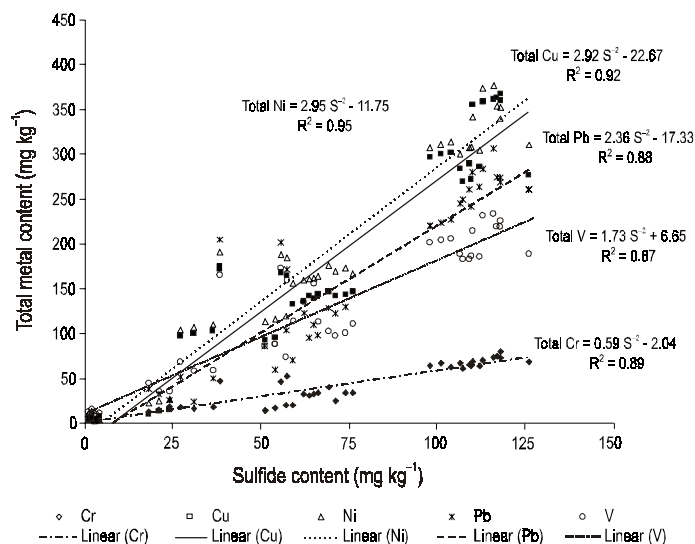


Figure 4. Variation of the total heavy metal content with the sulfide content. Regression and determination coefficient.

Figura 4. Variación del contenido de metales pesados con el de sulfuro. Regresión y coeficiente de determinación.

affect waters, fauna and flora, risking their entry into the trophic chain.

The effect of the fuel oil spill on polluted marsh soils was displayed by the Eh values and the low concentrations of Cr, Cu, Ni, Pb and V in available form, against high total contents, precipitated as sulfides.

The effects of the contaminant substances on the soils begin to weaken 500 m from the coastline. In spite of the correlation established between the distance to the coastline and heavy metal and total petroleum hydrocarbon content (table 5), in the first 400 m, there are important spatial variations

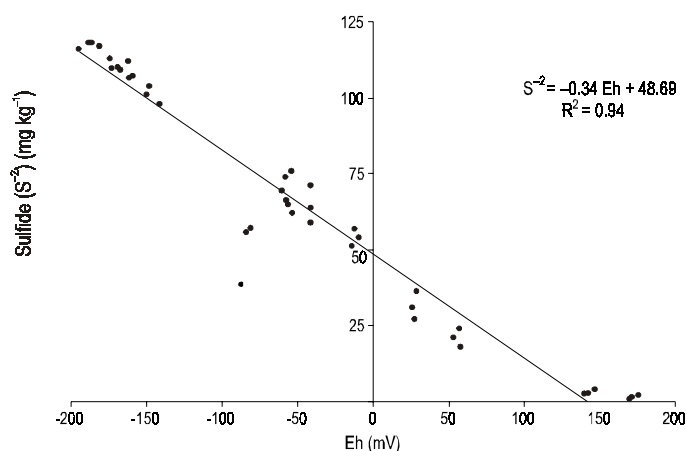


Figure 3. Variation of the sulfide content with the redox potential (Eh). Regression and determination coefficient.

Figura 3. Variación del contenido de S-S-2 con el potencial redox. Regresión y coeficiente de determinación.

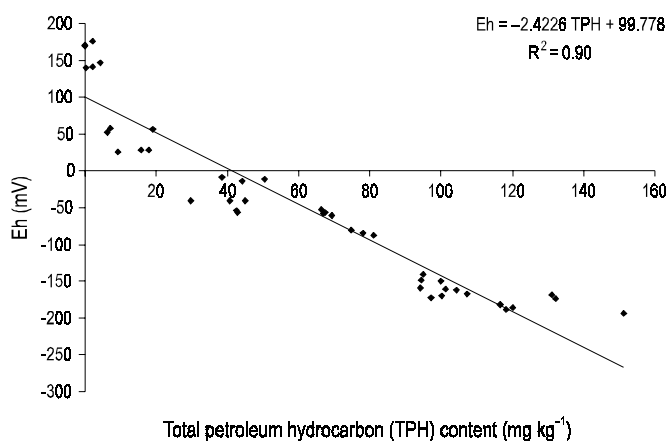


Figure 5. Variation of the redox potential (Eh) with the total petroleum hydrocarbon content. Regression and determination coefficient.

Figura 5. Variación del potencial red-ox con el contenido total de hidrocarburos.

El análisis estadístico realizado muestra que las diferencias entre los contenidos de metales pesados en los suelos no están relacionadas con su naturaleza y propiedades (tamaño de grano, contenido de materia orgánica).

Las correlaciones establecidas entre el potencial redox y el contenido de sulfuros, y entre éste último y los contenidos totales de Cr, Cu, Ni, Pb y V (figs. 3, 4) muestran que, a mayor reducción, los contenidos totales de metales aumentan porque permanecen en el suelo precipitados como sulfuros. También se ha establecido una estrecha correlación negativa entre el potencial redox y el contenido total de hidrocarburos (fig. 5, $r = -0.9$ y significativo para $P < 0.01$) que probablemente indica que el fuel provoca anaerobiosis e impide la oxidación de sulfuro a sulfato y la liberación de los metales pesados.

Así el potencial redox tiene un fuerte efecto en el contenido de Cr, Cu, Ni, Pb y V en forma insoluble. En la tabla 4 se aprecia que las concentraciones mayores se presentan bajo

because the metals and hydrocarbons penetrate into the soils through tidal action and not directly.

Finally, it must be noted that at several points in both marshes, there are very high total amounts of Cr, Cu, Ni, Pb, V and hydrocarbons (table 3). This may seriously jeopardize the fauna and flora if the acidic conditions allow part of these contents to become soluble. It must be highlighted that according to data provided by Andrade *et al.* (2002), the heavy metal content in the contaminated soils is about 50 to 200 times greater than the content in uncontaminated soils (control). This, in the near future, will have repercussions on the available amounts of heavy metal content and consequently the environmental quality of these areas.

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